California Environmental Protection Agency
AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for Acrolein Application Study

July 25, 2007

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The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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1.0 Introduction

The California Department of Pesticide Regulation's (DPR) memorandum dated January 29, 2007, "Proposed Toxic Air Contaminant Monitoring For 2007", requests that the Air Resources Board (ARB) conduct a comprehensive air monitoring study for acrolein during a waterway application.

This study will consist of three sampling periods; a background sample period, an application sampling period and a downstream sampling period. The background sampling period will be performed eight to twenty-four hours prior to injection of acrolein into the canal. The application sampling period will be conducted five minutes prior to the injection of acrolein into the canal, from the point of injection through to the end of the first mile. The downstream sampling period will be conducted between the 3.5 and 4.5 mile points when Baker Petrolite staff detect the presence of acrolein approximately 200 feet upstream of the first set of samplers in this group. There will be a total of 27 sample canisters (20 application, 2 background, 2 spares, 1 field spike, 1 trip spike, and 1 trip blank).

Background sampling will be conducted the day before the application on July 24, 2006, eight to twenty-four hours prior to the application. The field spike and two parallel background canisters on each side of the canal will sample for 4.5 $\pm$ 0.5 hours.

2.0 Project Goals and Objectives

The primary goal of this monitoring project is to measure the concentrations of acrolein in the ambient air during and after application.

To achieve the project goal, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.

2. Appropriate application of sampling/monitoring equipment to determine acrolein concentrations in the air adjacent to the application.

3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.

4. A final report containing all relevant information, data and results gathered in the course of MLD's activities during the planning and execution of this project.

3.0 Contacts

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4.0 Study Location

An acrolein application is planned for July 25, 2007, at the head of the Berenda Mesa irrigation canal in the Berenda Mesa Water District west of Lost Hills, CA.

5.0 Study Design

a) Background sampling will be conducted the day before the application on July 24, 2007, eight to twenty-four hours prior to the application and sample for 4.5 ± 0.5 hours. The background samplers will be located at Site 0W and Site 0E with one field spike located next to Site 0E. The field spike will be spiked with a concentration of 3-60 ppb of acrolein. The background sites will be located directly beside the discharge gate, just downstream from the injection point at the After Bay Reservoir outlet. The total number of background sample canisters will be 3. See figure 4 for approximate locations.

b) The acrolein application will be split between two one mile sections of the irrigation canal. The first section (0-1) starts at the injection point at mile 0 and ends exactly one mile from the injection point at mile 1. Four pairs of sampling sites will be located along the canal's edge at the following designated points; 0W & 0E, 0.3W & 0.3E, 0.7W & 0.7E and 1W & 1E. One pair of lateral sampling sites will be placed twenty meters from the sides of the second set of samplers designated 0.3WL & 0.3EL. Site 0E will have a collocated sampler. The total number of application sample canisters in section 0-1 will be 11. Sample duration will be 4.5 ± 0.5 hours. See figure 4 for approximate locations.

c) The second application monitoring section (3.5-4.5) starts at the 3.5 mile point and ends at the 4.5 mile point. Four pairs of sampling sites will be along the canal's edge at the following designated points; 3.5W & 3.5E, 3.8W & 3.8E, 4.2W & 4.2E and 4.5W & 4.5E. Site 3.5E will have a collocated sampler. The total number of application sample canisters in section 3.5-4.5 will be 9. Sample duration will be 4.5 ± 0.5 hours. See figure 5 for approximate locations.

d) The location of the acrolein injection point is located at the concrete and steel outlet of the After Bay Reservoir. The injection device will be placed through a grill over the top of the outlet. The injection plume will then continue under a road where it reaches the concrete discharge gate to the irrigational canal. The first pair of air sampling sites will be adjacent to the discharge gate and located on the west and east sides of the canal. The air samplers along the canal's dirt edge will be 3 to 10 meters from the water's edge. The four ambient sampling sites in each section on the east side of the canal will be 0.33 miles apart in the downstream direction. The lateral sites in the 0-1 section will be 20 meters from the sides of the second set of samplers. Due to the curvature of the canal the east side sampling sites will be used as a reference, so the eight samplers on the west side of the canal will be placed directly across from the east side ambient air samplers. All sampler intakes will be 1.7 meters (67 ±2 inches) above the ground.

e) Each sampling site will have at least one air sampler. The air sampler will consist of an evacuated Acculife-treated stainless-steel canister (6 liters capacity) drawing ambient air through a Restek Veriflo SC424XL passive flow controller. The air sample will be collocated at breathing-level (approximately 1.7 meters above the ground) using a ¼ inch diameter and 0.2 meters long Siltek® treated stainless-steel sample probe. The sample collection period will coincide with the four hour application period with a few additional minutes at each end for reduced exposure levels. The installed orifice flow controller will sample for approximately 4.5 hours at 13-16 cc/min.

f) In the 0-1 sampling section sample collection at the 0W, 0E & 0E-C will be initiated five minutes prior to the start of the injection (east and west side simultaneously). Staff will then drive to the next downstream samplers and simultaneously turn on each side's sampler. Staff will continue sequentially opening all canister-valves until all of 0-1 section's samplers are sampling. At the end of the application period, all valves will be sequentially closed in the same sequence as they were opened, flow controllers removed, sampling trees and canisters packed for delivery to Sacramento. Field notes and observations will be recorded (such as water temperature, water flow rate, acrolein application flow rate, and total amount of acrolein applied to water).

g) In the 3.5-4.5 sampling section, sample collection at the 3.5W, 3.5E & 3.5E-C will be initiated when Baker Petrolite staff detects the presence of acrolein at a point 200 feet upstream of the samplers. Staff will then proceed similarly to subsection f above.

h) Meteorological data will be collected using one Met One Instruments' AutoMet Digital Meteorological Monitoring System located within each sampling section. The AutoMets will be located between 8 and 20 meters from the water's edge on the same side of the canal. The exact locations will be determined during setup after sites are located that come the closes to meeting E.P.A. requirements. The meteorological sensors will be installed between 2.6 and 3.2 meters above the ground. The AutoMet station will continuously measure and record 5 minute averages for wind speed, wind direction, ambient temperature and percent relative humidity throughout the background and application sampling periods.

i) The MLD will provide DPR with a final report containing all relevant information, collected data and analytical results gathered during the course of the study.

j) Without a specific recommendation from DPR for the 2007 Acrolein study MLD is following Section C, "Air Monitoring Recommendations" of DPR's "Use Information And Air Monitoring Recommendations For The Pesticide Active Ingredients Acrolein" dated April 2006 when applicable.

6.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) staff will hand-carry canisters to and from MLD's laboratory in Sacramento, and to and from the sampling location. The canisters will not be exposed to extreme conditions or subjected to rough handling that might cause loss or degradation of sample.

At each sampling site, the operator will assure that the canister valve is closed and record the pre sampling information on the field sample report. The passive flow controller with sample probe will then be attached to the canister. Prior to any sampling the flows will be set to 15 $\pm$1cc/min. At the start of the application, the valves of all canisters will be sequentially opened and the start time and beginning vacuum reading on the controller's pressure gauge will be recorded. After 4.5 $\pm$0.5 hours the valves of all canisters will be sequentially closed and the stop time, stop flow and ending vacuum reading on the flow controller's pressure gauge will be recorded. Note that start and stop canister vacuum gauge readings rounded to the nearest whole number should be recorded in the "Comment Number" section of the "CANISTER FIELD LOG SHEET".

Sampling will occur as scheduled unless ambient conditions at the start include rain or instantaneous gusts of wind over 10 miles per hour. All reported sampling times, including meteorological data, will be reported in Pacific Standard Time (PST).

NLB will supply SPM with twenty seven (27) evacuated Acculife-treated stainless-steel canisters with individual shipping/protective boxes, (2 background, 20 application, 2 spares, 1 field spike, 1 trip spike and 1 trip blank). A data/sample tracking sheet, initiated by the lab, will accompany each canister. NLB will perform analyses for acrolein on all collected samples and report results to SPM in electronic form (Excel).

Laboratory analysis will be performed in accordance with applicable standard operating procedures (SOP MLD 066), "Standard Operating Procedure for the Determination of Oxygenates and Nitriles in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry". This analytical method currently has a Limit of Detection (LOD) of 0.3 ppbv (0.6 micrograms per cubic meter). SOP MLD 066 is included in this Protocol as Appendix A.

The following canister validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time**: Sample hold time criteria will be consistent with the laboratory's SOP MLD 066 stated 30 days.
2. **Duplicate Analysis**: Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Lab to provide duplicate analytical results and RPD.
3. **Method Detection Limit (MDL)**: MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions.
4. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be diluted and reanalyzed within the calibrated linear range.

7.0 List of Field Equipment

Quantity	Item Description
(2)	Met-One Auto met portable meteorology system with data logger which has calibrated sensors measuring 5 minute averages for wind speed, direction, ambient temperature, and relative humidity.
(1)	Measuring Wheel
(1)	200 ft measuring tape
(1)	Tripod and compass
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Alborg mass flow meter 0-100 ccm
(27)	Evacuated stainless-steel canister, each equipped with a vacuum/pressure gauge and a field data/sample tracking sheet, and carrying case (20 applications, 2 backgrounds, 2 spares, 1 field spike, 1 trip spike, and 1 trip blank).
(21)	Restek passive flow controller equipped with 8-hour orifices and 0.2 meter long, ¼ inch diameter, Siltek® treated stainless-steel sample probe.
(21)	Tripod, adjustable for mounting canisters with samplers.

Figure 1: Air Sampler – Canister with Passive Flow Controller

8.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards will be used to calibrate meteorological sensors and measure sample flow rates.

The sample flow rate of the passive flow controllers will be measured using mass flow meters having a current calibration certification and a range of 0-100 cubic centimeters per minute.

The metrological sensors will be calibrated and aligned following the procedures outlined in the standard operating procedures on the Air Monitoring Web Manual at the following link.

http://www.arb.ca.gov/aqdas/amwmn.php?c=5&t=sop

Each sample canister will be assigned a field data/sample tracking sheet that provides for identification of site, can ID number, operator, and sample information as well as sample tracking information.

Collocated (side-by-side) air samplers will operate at two sites during the application period. These collocated sites will be located at Site-0E and Site-3.5E.

Field Spike (FS): A field spike will be prepared by the laboratory by injecting a canister with a known volume and concentration of acrolein. The field spike canister will be coupled with a passive flow controller and will be collocated next to the background sampler at Site-0E. The field spike will sample for 4.5 $\pm$0.5 hours. The background is scheduled for the afternoon of July 24, 2007 8-24 hours prior to the acrolein application.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a canister with a known volume and concentration of acrolein and should be the same level as the field spike. The trip spike canister accompanies the sample canisters from the lab to the field but is not sampled.

Trip Blank (TB): A trip blank will be prepared by the laboratory. The trip blank canister accompanies the sample canisters from the lab to the field and returns but is not sampled.

Collocated (C): Collocated samples will be collected at sampling Site-0E and Site-3.5E during the application. Each will be sampling during its corresponding monitoring section time frame as the application samplers (4.5 $\pm$0.5 hours).

Valid samples are those that have a final canister pressure from **-12.0 “Hg** to **-4.5 “Hg**.

The acrolein sampling sites will be named accordingly for the background, application, and post application as follows:

Background Site Naming:

Site: 0W-B
Site: 0E-B
Site: 0E-FS

0-1 Application Section Site Naming:

Site: 0W	Site: 0E	Site: 0E-C
Site: 0.3W	Site: 0.3E	
Site: 0.3WL	Site: 0.3EL	
Site: 0.7W	Site: 0.7E	
Site: 1W	Site: 1E	

3.5-4.5 Application Section Site Naming:

Site: 3.5W	Site: 3.5E	Site: 3.5E-C
Site: 3.8W	Site: 3.8E	
Site: 4.2W	Site: 4.2E	
Site: 4.5W	Site: 4.5E	

Letter Abbreviations as follows

W = West Side
E = East Side
B = Background Sample
FS = Field Spike
C = Collocated Sample
WL = West Lateral Sample
EL = East Lateral Sample
TS = Trip Spike
TB = Trip Blank

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will insure accurate field and lab data collection.

9.0 Deliverables

9.1 Northern Laboratory Branch (NLB) Deliverables

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

1) Table(s) of sample to include:

   a. Sample identification (name).
   b. Date sample received from field.
   c. Date sample analyzed.
   d. Dilution ratio.
   e. Analytical results.

2) All equations used in calculating analytical results.

3) Table of duplicate results including calculated relative percent difference (RPD).

4) Table of collocated results.

5) Table of analytical results from all field, trip and laboratory spikes including percent recoveries.

6) Table of analytical results from all trip blanks.

7) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.

8) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.

9) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

10) Copies of each canister's data/sample tracking sheet which shall include the laboratory's final canister pressures. These pressures should indicate all canisters that were analyzed were between **-12 "Hg** to **-4.5 "Hg**.

9.2 Air Quality Surveillance Branch Deliverables

Within 60 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

1) Sampling Protocol.

2) Personnel Contact List.

3) Site Maps.

4) Site Photographs.

5) Site Descriptions and Measurements (site, sampler, GPS coordinates, inlet height, distance to roads, site-specific comments, water temperature, water flow rate, acrolein application flow rate, and total pounds or gallons of acrolein applied to water).

6) Sample Summary Table.

7) Field Log Sheets.

8) Laboratory Analysis Reports with calculations in electronic format.

9) Met Station and Sampler Calibration Reports.

10) Transfer Standards' Certification Reports.

11) Disk containing electronic files of 5-minute averaged Meteorological Data.

12) Disk containing electronic files of Report.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

[Place data sheet inside plastic pouch]

CALIFORNIA AIR RESOURCES BOARD
SUMMA Canister Pesticide Data/Sample Tracking Sheet

Pesticides
Veriflo
Controller

Project Name: _____

Site/Sample Name: _____

Lab I.D.: _____ Operator & Agency: _____

			CANISTER		LABORATORY	SAMPLER			
	Date	Time (PST)	Vacuum ("Hg)		Pressure or Vacuum	MFC Reading			
			LAB	FIELD				Vacuum	
Set-Up									
Start									
Stop					LAB**				

Type of Sample: [ ] Regular [ ] Collocated [ ] Spike [ ] Blank [ ] Other

Field Log Number: _____ Canister ID Number: _____ Sampler ID Number: _____

Observed Unusual Sampling Condition: [ ] Wind-Blown Sand/Dust [ ] Rain [ ] Farming Nearby [ ] Construction Nearby [ ] Fire Nearby [ ] Other _____

[ ] INVALID SAMPLE INFORMATION

Reason for Sample Invalidation

[ ] Vacuum lower than -12"Hg
[ ] Vacuum higher than -4"Hg
[ ] Sampling period out of range (<___ or >___ hours)
[ ] Other reasons: _____
[ ] Sampling equipment inoperative

Field Comments: _____

Sample Tracking

Action	Transfer Method (Check one)		Name & Initials	Date/Time
	Carrier	Person		
Released by Lab				
Received by Field				
Released by Field				
Received by Lab				

===FOR LABORATORY USE ONLY====

Lab Comments: _____

** = Calibrated Guage Pressure or Vacuum

07/13/07

Figure 2: SUMMA Canister Pesticide Data/Sample Tracking Sheet

CANISTER FIELD LOG SHEET																
Project: Acrolein Ambient Air Monitoring In Kern County																
Start Flow Set: 17 to 16ccm End vacuum Criteria: -12 to -4"Hg																
		Sampler	Date & Time		Canister Vacuum		Mass Flow		Corrected		Weather					
Log	Sample	ID	Entry Example (6/14/07 13:42)		Display		Meter Display		Average	Comment	K,P,C,F&R		Initials			
#	Name	Number	Start	End	Start	End	Start	End	Flow	Number	Start	End	Start	End		
	MFM Used #:		Slope:		Intrcpt:											
1 of 4				Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)												

Figure 3: Canister Field Log Sheet

Figure 4: Berenda Mesa Canal Acrolein Section 0-1 Sites

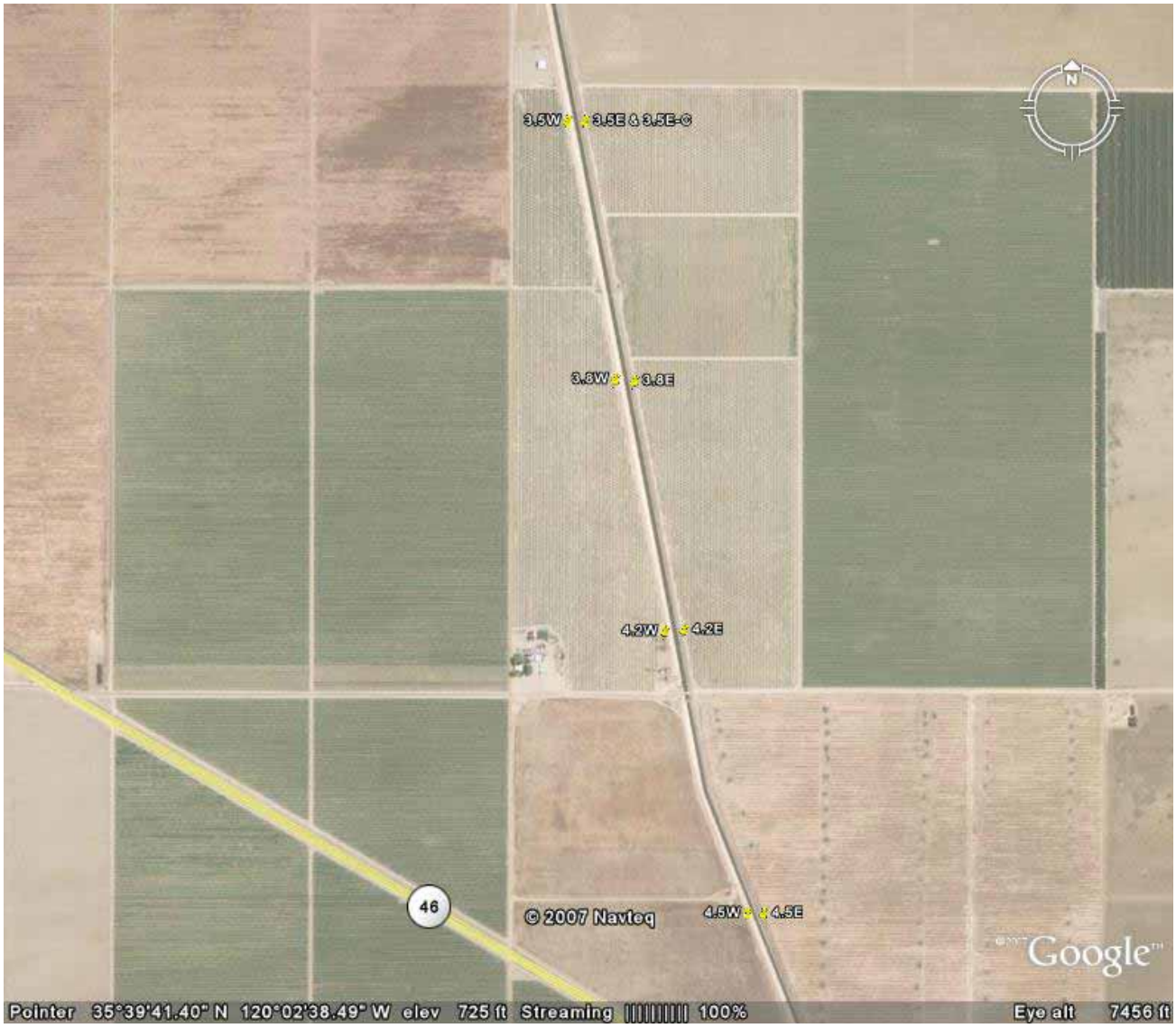

Figure 5: Berenda Mesa Canal Acrolein Section 3.5-4.5 Sites

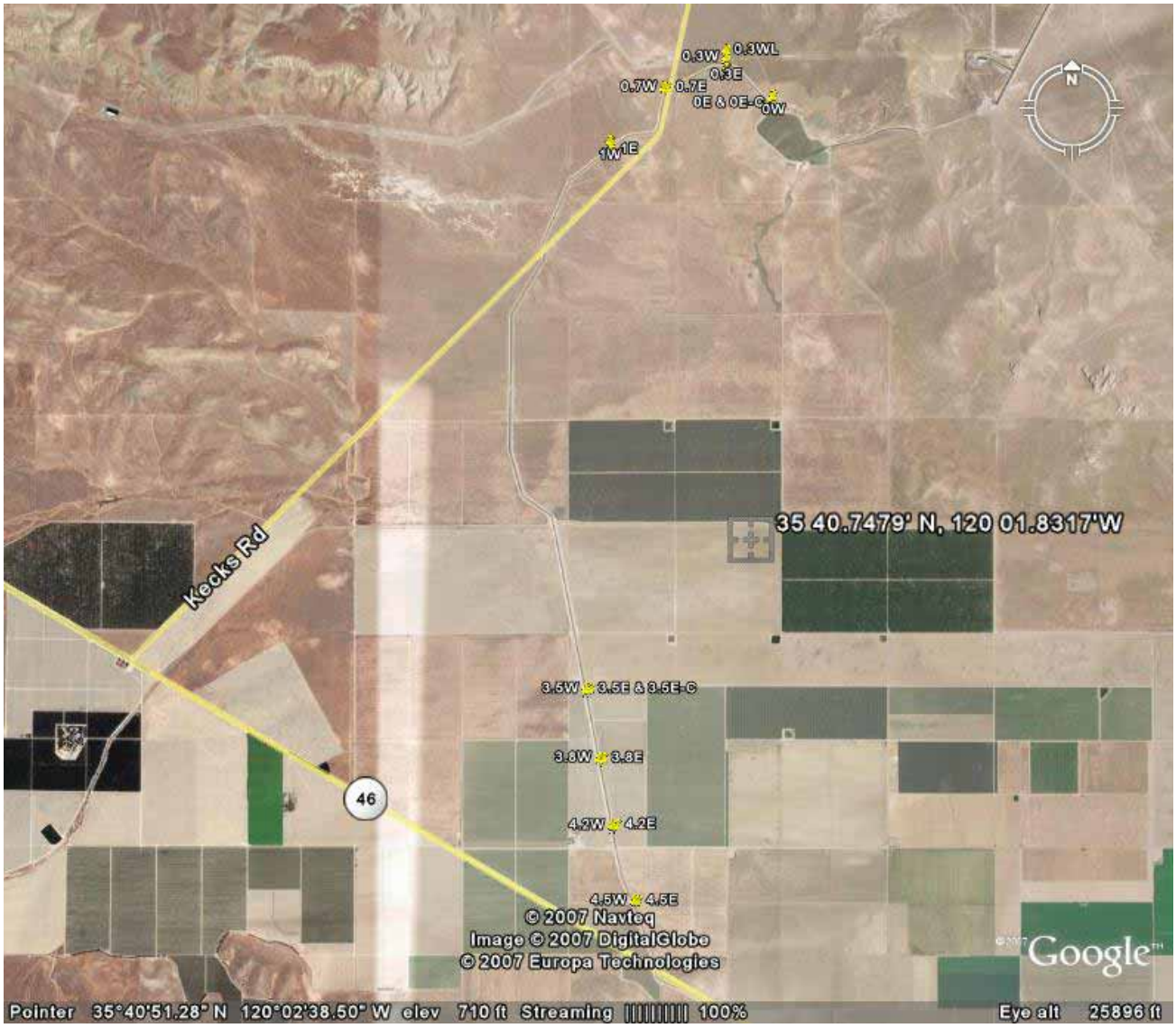

Figure 6: Berenda Mesa Canal Acrolein Sites Overview

APPENDIX A: STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF OXYGENATES AND NITRILES IN AMBIENT AIR BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The Organics Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for acrolein collected by the canister method. This analytical procedure is entitled, "Standard Operating Procedure for the Determination of Oxygenates and Nitriles in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" and due to its size can be found at: http://www.arb.ca.gov/aaqm/sop/sop_066.pdf